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SUMMARY OF RADIATION EFFECTS ON THERMIONIC INSULATOR MATERIALS

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SUMMARY OF RADIATION EFFECTS ON THERMIONIC INSULATOR MATERIALS

by John T. Mayer
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SUMMARY

Nuclear thermionic power systems are presently being studied for possible space applications. One of the critical materials in such designs is the metal oxide ceramic used as an electrical insulator and seal between various components. Such materials must withstand high temperatures (1000°C and above) as well as fast neutron doses to 10^{22} neutrons per square centimeter. To gain insight into their behavior in such an environment, a literature survey has been conducted for radiation effects data on the following candidates: beryllia, alumina, thoria, zirconia, and yttria. The properties of interest include dimensional changes, thermal and electrical conductivity, strength, thermal expansion coefficient, elastic modulus, and breakdown voltage.

A large amount of data were found on beryllia, but much less work has been done on the other oxides, especially zirconia, thoria, and yttria. Beryllia seemed to be the most promising material, and its radiation stability may be improved by the use of additives and/or fine-grained low-density material. However, the large gas production rate in beryllia may restrict its use in thermionic systems; the release of a significant amount of helium gas into the interelectrode space may affect converter performance. The most successful tests on beryllia to date showed relatively minor changes after fast neutron doses to 9×10^{21} neutrons per square centimeter at 1000°C . In contrast, high-temperature tests of alumina and yttria have resulted in gross fracturing at lower doses. No high-temperature, high-dose data on thoria or zirconia were found.

INTRODUCTION

In recent years, increased attention has been given to the thermionic emission process for space auxiliary power application. The simplicity of the basic process is a decided advantage in a system that must perform unattended for long time periods. Within each thermionic diode or cell, generation of electricity is obtained by heating a cathode (emitter) to release electrons, which are subsequently collected at an anode

(collector). The interelectrode space is usually filled with an ionized gas such as cesium to neutralize the space charge that would otherwise build up near the emitter. Each diode develops a potential of about 1 volt and can deliver a relatively high current to an externally connected load. A thermionic power system employs several hundred such diodes in various series and parallel connections in order to obtain the desired voltage and power levels.

Physical and electrical separation of series-connected diodes as well as electrodes within each diode must be provided. In addition, this insulation is often part of the cesium containment envelope and must therefore be an effective seal. The high temperatures required for efficient thermionic operation (emitter temperatures are as high as 2000°C) mean that metal oxide ceramics must be used for the insulation.

Thermionic power systems place severe requirements on the ceramic insulator materials. They must provide insulation and sealing over periods of up to 2 years in an environment including temperatures in excess of 1000°C and cesium vapor. The property requirements include high electrical resistivity and breakdown voltage, high-thermal conductivity, low vaporization rate, high strength, a coefficient of expansion similar to the refractory metals involved, and chemical compatibility with the refractory metals and cesium. The primary candidates for thermionic diode insulators are beryllia (BeO) and alumina (Al_2O_3), while thoria (ThO_2), zirconia (ZrO_2), and yttria (Y_2O_3) have also been considered. All of these ceramic oxides satisfy the property requirements to some degree, although variations for a particular property can be large.

Thermionic systems employing a nuclear reactor as the emitter heat source are presently under study. In some designs, the thermionic diodes form an integral part of the reactor core. In this case the insulator materials must satisfy an additional requirement, that is, they must retain the properties mentioned previously after fast neutron doses¹ as high as 10^{22} neutrons per square centimeter ($\text{neutron}/\text{cm}^2$). A knowledge of their radiation behavior is essential to the design of an inpile thermionic power system.

The purpose of this report is to summarize the pertinent data in the literature on the effects of nuclear radiation on the candidate materials for thermionic insulator application. Although radiation effects summaries have been published for some of the individual materials, none include the most recent work at high doses and temperatures. Furthermore, no thorough summary for thermionic application is available which in-

¹The term "dose" will herein be used to denote integrated neutron flux (fluence), expressed in $\text{neutrons}/\text{cm}^2$. For gamma radiation, "dose" will denote the integrated gamma exposure rate, expressed in $\text{R}(\text{C}/\text{kg})$. The term "flux" will be used to denote the neutron particle flux only, expressed in $\text{neutrons}/(\text{cm}^2)(\text{sec})$. The term "dose rate" will denote the gamma field exposure rate, expressed in R/hr or $\text{C}/(\text{kg})(\text{hr})$. All neutron fluxes and doses refer to energies $\geq 1\text{ MeV}$ ($1.6 \times 10^{-13}\text{ J}$) unless otherwise noted.

cludes all the main candidate materials. Of primary interest are the effects on the pertinent physical properties at the temperatures and doses anticipated in an actual thermionic system. Where such information is not available or is incomplete, results of related studies will be reported. These include property changes in other environments (of temperature and radiation), annealing experiments, and analytical work. A brief summary of basic radiation-damage mechanisms for the oxides is also included.

Although an attempt has been made to review all pertinent information on the subject, especially that published during the last 5 years or so, it is certain that some results have been omitted. This is primarily due to a lack of availability or to the classified nature of certain work.

SYMBOLS

A, A_{vs}	constants defined in text
E	modulus of elasticity, psi; N/m^2
K	thermal conductivity, $Btu/(hr)(ft)(^{\circ}F)$; $W/(m)(^{\circ}K)$
k	Boltzmann constant, $1.38 \times 10^{-23} J/^{\circ}K$
P	gamma dose rate, R/hr ; $C/(kg)(hr)$
Q	volumetric heating rate, $Btu/(in.^3)(sec)$; W/cm^3
r	cylinder radius, in.; cm
T	temperature, $^{\circ}K$; $^{\circ}C$
t	irradiation time, sec
U	energy defined in text
$\Delta V/V$	volume change, percent or fraction of original
α	linear thermal expansion coefficient, $^{\circ}K^{-1}$
γ	Poisson's ratio
ρ	electrical resistivity, ohm-cm
σ	electrical conductivity, $1/\rho$, $ohm^{-1}-cm^{-1}$
Φ	neutron flux, neutrons/ $(cm^2)(sec)$

Subscripts:

a	measured at axis
i	initial value, before irradiation

- f final value, after irradiation
s measured at surface

BASIC RADIATION-DAMAGE PROCESSES IN CERAMIC OXIDES

Before considering radiation-induced changes in physical properties, it is of interest to examine the basic radiation-damage processes in the oxides. A knowledge of such processes can be helpful in understanding the changes, resolving discrepancies, and supporting conclusions. This section will briefly outline the basic mechanisms of defect production in all oxides, and consider the possible effects on microstructure and properties of interest. It will also consider the possible effects that ceramic material variables might have on radiation stability from the microstructure standpoint. The peculiarities of each oxide will be considered separately in later sections.

A large amount of study has been directed at understanding the basic radiation-damage processes and their immediate effects in ceramic oxides. This has been done primarily on BeO, Al_2O_3 and other oxides not necessarily of interest as thermionic insulators (e. g. , MgO, SiO_2). Although the basic damage mechanisms and defect behavior are similar for all oxides studied, the resultant effects on microstructure (and therefore physical properties) are quite variable. This is due mainly to the different crystal structures and elements involved in the materials.

The primary processes during irradiation are: (1) the production of helium or other gas atoms by (n, α) or other neutron reactions; (2) the production of "free" electrons by gamma radiation; and (3) the production of point defects (interstitial atoms and vacancies) and small clusters of defects by fast-neutron collisions. The defects so formed are quite mobile, especially at high temperatures. This mobility results in two further processes: self-annealing (returning to the original state) and agglomeration (formation of larger complex defects or bubbles).

For the case of gas atoms, self-annealing does not occur (except for diffusion of gas atoms out of the material), and agglomeration into bubbles is the important process. For gamma-produced electrons, on the other hand, agglomeration does not occur. Instead, an equilibrium electron concentration results from their constant production rate and fast recombination rate. This equilibrium is reached soon after the gamma field is present and is independent of gamma dose (ref. 1). For point defects, both self-annealing and agglomeration occur and compete with each other. A large amount of point defect recombination takes place within a short time after the atoms are displaced. It has been estimated that although 10^3 or so interstitial-vacancy pairs can be formed by a high-energy neutron, the number remaining after initial self-annealing is of the order

of 10 (e. g., see refs. 2 and 3). These remaining defects subsequently diffuse through the lattice and may undergo further recombination or agglomeration into larger complexes such as dislocation loops or vacancy cavities.

The three mechanisms of production of defects described previously and their subsequent behavior are influenced by one or more of the environmental variables of radiation characteristics, time, and temperature. Although the free electron concentration is mainly dependent on gamma dose rate alone (ref. 1), the other processes are influenced by all of these variables.

In the environment experienced by a thermionic diode insulator, the defects produce various changes in the microstructure of the materials. The most universal and probably most important microstructure change caused by radiation is the expansion of the individual grains or crystallites in the material. This can result from point defects, clusters of point defects, and gas atoms in the normal crystal lattice. Depending on the crystal structure involved, this expansion may be anisotropic, that is, one dimension of the grain may expand more than another. In any case, it may eventually (at a high enough dose) lead to microcracking, either across the grain (transgranular) or along the grain boundary (intergranular). In the oxides being considered, transgranular cracking is generally less important than grain-boundary separation, and the term "microcracking" will hereinafter denote the latter form, unless otherwise noted. Another important microstructure change caused by radiation is the formation of gas bubbles within the grains or along grain boundaries because of gas atom agglomeration. Although this may or may not contribute to the grain expansion, gas bubbles at the boundaries can reduce grain-boundary strength, and thus lower the material's resistance to microcracking.

In the absence of microcracking, property changes in irradiated ceramic oxides are generally small. A macroscopic volume expansion directly related to the grain expansion does occur, but this is only a few percent at most. Strength often increases or may decrease slightly. Probably the most significant property change in nonmicrocracked structures is in thermal conductivity. It will decrease because the orderly lattice structure has been disturbed by various defect clusters, bubbles, and voids. There is also the possibility that these and other property changes in nonmicrocracked specimens will saturate in time (if gas production is small) when the defect annealing rate equals the production rate. However, when microcracking occurs, properties begin to degrade at a much faster rate. Gross volume expansion increases until the material is fractured or powdered. Strength and thermal conductivity undergo large decreases.

Microstructure effects on electrical properties are not as well known as for the other properties. Although the gamma-induced free electron concentration can be determined with some accuracy, the effects of microstructure on mobility are not well known. This also applies to the breakdown voltage, which is further complicated by a dependence on the thermal conductivity. One would expect, however, that any disruption of the nor-

mal lattice order would decrease charge carrier mobility and consequently decrease electrical conductivity.

The radiation-induced property changes in ceramic oxides are further complicated by material variables, as well as the environmental factors mentioned previously. These include processing techniques and what may be called end-product characteristics. The various methods of preparing ceramics, such as pressing, sintering, extruding, and flame-spraying, may affect grain-boundary strength and cause preferential orientation of grains. The resulting grain size, density, and purity will determine to a large extent the material's resistance to microcracking. The grain size will determine the total grain-boundary area, which will affect microcracking characteristics and may also influence gas diffusion and agglomeration. Higher porosity may reduce the expansion due to gas atoms since gas can diffuse to and agglomerate in voids in the material. Grain-boundary characteristics may also be affected by certain types of additives. These may allow the grains to expand more freely and also may influence gas diffusion.

In summary, the basic damage-producing mechanisms are at least qualitatively understood, but their effects on physical properties are complicated by various environmental and material factors. The result of this is often a large discrepancy in radiation test results of the same oxide.

RADIATION EFFECTS IN BERYLLIA

The interest in beryllia as a neutron moderator has generated a large amount of data on its behavior in a radiation environment. These data cover a wide range of sample characteristics and environmental variables, as well as experimental techniques. Both property changes and basic mechanisms have received a great deal of attention.

Several summaries of radiation effects on BeO have been published. Probably the most recent is that included in a general review of BeO for reactor application by Simnad, Meyer, and Zumwalt (ref. 4). Brief descriptions of recent work up to about mid-1965 are given, covering annealing studies, radiation damage mechanisms, and property changes. Kircher and Bowman (ref. 5) present an extensive survey of all aspects of BeO work up to mid-1962. Both of these references refer to prior surveys in the field.

Radiation-Damage Mechanisms

The extensive work on beryllia has resulted in a fairly good picture of the important mechanisms occurring during irradiation. It has been found that volume expansion with

microcracking can occur to a significant degree. The major causes of this expansion and microcracking are helium gas formation and a highly anisotropic grain expansion.

A relatively large amount of helium gas is formed in BeO (ref. 6), primarily through the (n, 2n) reaction in beryllium. The agglomeration of the helium atoms into bubbles is primarily a high-temperature phenomenon, being generally unimportant below about 500⁰ C (refs. 7 to 9). After high-temperature irradiation, bubbles as large as 0.5 micron have been observed along grain boundaries, although a significant amount is retained within the grains. The importance of these bubbles on gross volume expansion is still disputed by some experimenters, although different testing environments may account for the disagreement. Collins (ref. 10) estimated that after irradiation to 2.5×10^{21} neutrons/cm² at 1000⁰ C, about 60 percent of the volume expansion of BeO samples was due to helium bubbles. This is corroborated to some degree by lower dose experiments. Clarke and Wilks (ref. 11) point out that, although there is no firm evidence that the gas actually contributes to growth, it is probable that it does. On the other hand, Pryor and Hickman (ref. 12) state that little of the expansion at 900⁰ to 1000⁰ C can be attributed to helium bubbles.

The bulk of the anisotropic grain expansion in BeO irradiated at high temperatures is generally attributed to large defect clusters (e. g. , see refs. 8, 10, 13, and 14). These clusters are planar arrays of interstitial atoms (dislocation loops) primarily perpendicular to the c-axis of the hexagonal BeO crystal lattice. Smaller defects, including point defects, also contribute to the grain expansion by causing anisotropic lattice expansion. However, this contribution is quite small at higher irradiation temperatures. The total anisotropic grain expansion, if large enough, can result in grain-boundary separation (which is possibly enhanced by helium bubbles). The production and growth of the dislocation loops under irradiation has been studied extensively using electron microscopy. Several investigators (refs. 8, 11, and 15) have found that irradiation at 1000⁰ C produces loops ranging from 500 to 2000 Å (0.05 to 0.2 μm) in diameter which are quite stable. Annealing experiments (ref. 11) show that some loops persist even to 1800⁰ C. Some correlation between the loop density and the macroscopic growth has been found by Wilks and Clarke (ref. 14), but such correlations are difficult at high doses because of the high density of these loops. Their microscopy studies (ref. 11) have also revealed relatively large cavities within the grains which seem to be a high-dose phenomenon ($>10^{21}$ neutrons/cm²). These cavities probably contain a significant amount of the helium gas formed. Similar studies of helium bubbles at grain boundaries by Collins (ref. 10) indicate that grain size has a significant effect on the size and number of bubbles.

Influence of Material and Environmental Factors

Many radiation studies of polycrystalline BeO have yielded information on the effects of material variables and environmental factors on its radiation behavior. The parameters examined have included various processing techniques, several additives, a wide range of grain size and density, neutron flux, and temperature. Because of the many parameters involved and the fact that all seem to affect radiation stability to some degree, great care must be taken in drawing conclusions from the data. Only in rare cases is one parameter varied with all others held constant. In addition, it is not always clear that a conclusion from a particular test will be true for all conditions. For example, the effects of a material variable on radiation behavior in a low-temperature test are not necessarily applicable at higher temperatures. Generally, one must relate the parameter in question to a particular mechanism and study its behavior under different conditions before extrapolating.

Despite the diversity in samples and environments, some general criteria for obtaining better performance from BeO have evolved and are discussed in the following paragraphs. They may not be very quantitative, but seem to be well-founded and applicable under most conditions.

Considering first some of the processing techniques, it has been found by at least three different groups (refs. 7, 10, and 16) that hot-pressed (HP) BeO showed less radiation stability than cold-pressed/sintered (CP/S) samples. This was evidenced by a greater volume expansion and a lower threshold dose for microcracking and gross fracture for HP BeO. Figure 1 illustrates this for two otherwise similar samples. There is also an indication of better resistance to microcracking by extruded/isostatically pressed (E/IP) samples (ref. 10). This better performance is attributed to the preferred grain orientation, which reduces the amount of grain-boundary separation for a given dose and expansion.

Several groups have examined the effects of grain size and density (or porosity) on radiation resistance. The results of grain size investigations have provided ample evidence that small-grained samples will perform better under all conditions (e.g., see refs. 7, 9, 17, and 18). This applies throughout a range of grain sizes from 1 to 100 microns. Figure 2 illustrates the effects of grain size on volume expansion, which is probably the best criterion for radiation damage. Also shown is the effect of density for two sets of data with comparable grain sizes (the 5- μm samples and the 17- and 25- μm samples). The behavior shown is typical of results obtained in most investigations; that is, low-density (about 2.6-g/cm³) samples generally performed better than high-density (about 2.9-g/cm³) types, at least in volume expansion (refs. 9, 18, and 19). Collins (ref. 19) has found at least a qualitative explanation for the improved stability of low-density, small-grain-size samples. He found helium bubbles to be smaller and less

numerous for smaller grain sizes and postulates that a larger void fraction in low-density samples may also relieve the helium accumulation problem.

There is good general evidence that certain additives may also improve the radiation resistance of pure BeO (e. g. , see refs. 17 and 20). Although the effects of additives have not been given widespread attention, at least one thorough study has been made which examined several additives in 0.5 to 2 percent concentrations. Collins (ref. 10) found improved microcracking resistance for an $\text{Al}_2\text{O}_3/\text{SiO}_2$ additive and for bentonite (a montmorillonite clay) in small-grain-size E/IP BeO. Other additives were found to have no effect or detrimental effects on the radiation stability of BeO.

The effects of irradiation temperature on BeO damage are relatively well-known over the range of 100° to 1100° C. With few exceptions, performance is much better at higher temperatures. Collins (ref. 10) found that the threshold dose for microcracking at 1000° C is about 20 times that at 100° C. Most other properties are similarly affected, notably volume expansion and thermal conductivity. This is to be expected because of the more rapid annealing of the defects produced under irradiation. The marked dependence of radiation damage on temperature is probably the primary source of difficulty in comparing individual test results. Relatively minor differences in temperature (or errors in its measurement) can result in false conclusions with respect to the other variables being examined.

The question of neutron flux effects is still unresolved. The experimental data that can be directly compared are limited, and the questionable role of helium gas further complicates matters. Two groups have concluded that there is no major flux effect. Hickman and Chute (ref. 8) based this on data below 700° C and at neutron doses below 2×10^{21} neutrons/cm² over the flux range of 10^{13} to 3×10^{14} neutrons/(cm²)(sec). Keilholtz, Lee, and Moore (ref. 18) also found no flux effect in X-ray diffraction measurements after similar doses at a flux of 0.6 to 2.4×10^{14} neutrons/(cm²)(sec) and at temperatures of 650° and 1100° C. Other groups, however, have found a saturation of volume expansion with dose at high irradiation temperatures ($>800^\circ$ C) which compared well with analytical expressions dependent on flux (refs. 10 and 12). According to these expressions, the expansion (not including helium) should, after long irradiation times, approach an equilibrium value which is larger for higher fluxes.

Property Changes Under Irradiation

The effects of material and environmental variables discussed in the previous section must be kept in mind when examining the actual changes in physical properties due to radiation. In this manner one can separate the "good" data from that obtained under less realistic conditions or with less ideal samples. In addition, one can, in some

cases, extrapolate from less ideal data. This is especially important when there is a lack of data under certain conditions of interest, for example, high temperature. Although high temperature (say 900° to 1100° C) behavior is of primary interest, some data at lower temperatures will be included where necessary or informative.

Table I lists some of the out-of-pile property values for BeO as well as the other oxides. The ranges listed give an indication of the importance of material variables in determining the behavior of these oxides.

Volume expansion. - The property given most attention in BeO radiation tests is macroscopic volume expansion. To date, the highest dose test (by Collins, ref. 19) has shown that BeO can withstand neutron doses of 9×10^{21} neutrons/cm² at 1000° C with little or no microcracking and a total volume expansion of 3 to 5 percent. The samples were either pure BeO or BeO containing MgO additive with grain sizes of about 5 microns. As shown in figure 2, expansion was quite different for the two densities examined. The expansion seemed to be reaching a limiting value at about 3 percent for the low-density samples (2.6 g/cm^3), in contrast to similar samples of higher density (2.9 g/cm^3) which showed a linear increase in expansion to 5 percent at 9×10^{21} neutrons/cm². In general, other high-temperature, high-dose tests have not been as successful. Keilholtz, Lee, and Moore (ref. 18) noted microcracking and minor fracturing at 2×10^{21} neutrons/cm² and 1100° C, although the volume expansion was relatively constant at 2 percent over the dose range of 1 to 4×10^{21} neutrons/cm². The samples used were of low density (2.7 g/cm^3) and medium ($17 \text{ }\mu\text{m}$) grain size. A series of tests by Tobin (ref. 20) on many types of BeO at 810° to 970° C and a dose of about 2×10^{21} neutrons/cm² resulted in several cracked samples. However, most of these were attributed to fabrication flaws. Volume changes of most samples were small, and generally fell within the 2 percent accuracy of the measurements. Desport and Smith (ref. 21) found an expansion of approximately 2 percent at an even lower dose (4×10^{20} neutrons/cm²) in a 1000° C irradiation. However, the samples were hot-pressed and had high density and large grain size.

Strength. - Strength changes of BeO during irradiation follow a pattern similar to many materials. That is, a strength increase first occurs, after which the strength decreases until failure of the sample. The strength decrease in BeO as dose increases is generally indicative of the onset of microcracking. For Collins' samples described previously (irradiated to 9×10^{21} neutrons/cm² at 1000° C), strength retention was good. The low-density samples retained 60 to 80 percent of their original strength, while higher density samples had strength values which were greater than the unirradiated value (ref. 19). Tobin (ref. 20) found a 60 to 80 percent reduction in crushing strength, after a dose of 1.7 to 2.1×10^{21} neutrons/cm² at 800° to 980° C, on 22 samples of varying composition and grain size. Data scatter was quite large even for nominally identical conditions, which made correlations with microstructure difficult. Little other data

seem to exist on BeO strength properties after high-temperature irradiation.

Thermal conductivity. - Thermal conductivity has also received less attention than gross fracture and expansion. Collins (ref. 10) found a conductivity decrease of 7 percent at 1000°C after irradiation to 2.5×10^{21} neutrons/cm². He also found that the percent decrease was somewhat greater if measured at lower temperatures after irradiation at 1000°C . This result is helpful in interpreting the results of Tobin (ref. 20), who irradiated specimens at high temperatures but made thermal conductivity measurements at a lower temperature. For 22 samples irradiated at about 2×10^{21} neutrons/cm² and 800° to 980°C , the ratio of post- to pre-irradiation thermal conductivity at 550°C was 0.37 to 1.27. The average ratio was approximately 0.7, which compares well with Collins' results (ref. 19). Measurements of thermal conductivity against temperature for other irradiation temperatures are shown in figure 3. Since annealing affects were minimal during the measurements, it is believed that the larger changes in conductivity at lower measuring temperatures are a result of the actual defect structure following irradiation. It has been found in all cases that thermal conductivity changes are relatively small until significant microcracking occurs.

Electrical properties. - Little experimental work has been done on the changes in electrical properties of BeO under irradiation. The effects of high gamma dose rates and high neutron doses are essentially unknown. Davis (ref. 1), studying the effects of γ -radiation on electrical properties, found no change in the breakdown voltages of BeO above room temperature in a reactor gamma field of 2×10^3 roentgens per hour (0.516 C/(kg)(hr)). In another test, he found a decrease in the electrical resistivity at temperatures below about 600°C because of a 5×10^6 roentgens per hour (1.29×10^3 C/(kg)(hr)) dose rate, as shown in figure 4. However, the radiation had no effect at higher temperatures. (The neutron environment was not reported, its effect being considered insignificant in these experiments.) The effects of neutron dose on electrical resistivity were studied by Patrick (ref. 22), who found a large decrease after irradiating to 2.8×10^{20} neutrons/cm² at 520°C . The original resistivity was not given, but the value after irradiation was 3.89×10^4 ohm-centimeters. After irradiation to 2.84×10^{20} neutrons/cm² at about 900°C , Elston, Frisby, and Labbé (ref. 23) found that the resistivity decreased by 10^2 to 10^3 ohm-centimeters at 500°C ; however, the original value was recovered after annealing at 900°C .

Expansion coefficient. - A few results of thermal expansion coefficient measurements have been reported. Collins (ref. 9) irradiated BeO samples to 1.5×10^{21} neutrons/cm² at 1000°C , while Walker, Mayer, and Hickman (ref. 24) irradiated to 4.6×10^{20} neutrons/cm² at 650° to 690°C . Both reported no significant change in expansion coefficient due to irradiation.

RADIATION EFFECTS IN ALUMINA

Radiation damage work on alumina has not been as extensive as with beryllia, and its performance has not been as good as that of beryllia. Especially scarce are data on property changes at high doses and high temperatures ($\geq 800^{\circ}\text{C}$) and information on the effects of material variables. It becomes necessary to rely on low-temperature data and mechanism studies in order to compare alumina with other materials and determine its behavior at high temperatures. One of the reasons for the lack of high-temperature data is the more frequent occurrence of gross fracturing at these temperatures. This may be due to thermal effects, a subject to be examined in a later section.

There do not seem to be any recent summaries of radiation tests on alumina. The best general survey appears to be that of Kircher and Bowman (ref. 5).

Radiation-Damage Mechanisms

Although the radiation stability of alumina seems to be somewhat less than that of beryllia, a comparison of radiation-damage mechanisms does not explain this. It has been found that the two oxides are quite similar in the formation of large planar defect clusters and cavities during high-temperature irradiation (refs. 11 and 25). Other similarities are the small lattice expansion at high temperature and the comparable concentrations of gamma-produced free electrons. In other respects, however, damage in alumina appears to be less drastic. In the first place, although helium production does occur, it is low. Wilks' calculations (ref. 6) show that the gas produced in alumina is less than that in beryllia by a factor of 180. Furthermore, the large anisotropic expansion occurring in BeO is not found in Al_2O_3 . Although the crystal structure is hexagonal like BeO, and some anisotropy would be expected, the largest anisotropic ratio (defined as the ratio of the fractional increases in the c and a lattice parameters) measured to date is 3.8 (ref. 26), compared with values as high as 20 for BeO (ref. 27). Anisotropic expansion in alumina is largest for the high-density translucent type (Lucalox). The value of 3.8 mentioned previously was obtained by Kelholtz, et al. after irradiation to 1.4×10^{21} neutrons/cm² at about 100°C . They also measured values of 2 to 3 after irradiation to doses of 0.6 to 5.2×10^{21} neutrons/cm² at temperatures from 300° to 600°C (refs. 27 and 28). Other forms of alumina, including medium- and high-density forms and single crystals, have shown much lower values for the anisotropic lattice expansion (refs. 3, 26, and 29 to 31). This includes a test at 800°C and 4×10^{21} neutrons/cm² by Kelholtz, Lee, and Moore (ref. 30), where the expansion was nearly isotropic.

Grain-boundary separation was found in the tests at 300° to 600°C mentioned previously (refs. 27 and 28). It began at a dose of about 2.3×10^{21} neutrons/cm² and was

extensive at 4.7×10^{21} neutrons/cm². Since lattice expansion contributed little to the macroscopic expansion at higher doses, it was postulated that the large defect clusters were important in contributing to the anisotropic expansion and resultant microcracking. It was also noted that the amount of microcracking seen in Al₂O₃ at 4.7×10^{21} neutrons/cm² was similar to that in BeO at doses lower by a factor of 5 to 10 (see also ref. 9).

These results imply that from the standpoint of microscopic damage, the radiation stability of alumina should be better than that of beryllia. Helium production is much less, anisotropic lattice expansion is smaller, and microcracking, when it does occur, has a much higher threshold dose.

Influence of Material and Environmental Factors

Very little data exist on the effects of material variables on alumina radiation damage. Additives have evidently not been examined at all. The work that has been done indicates that material variables have no significant effects on property changes. However, some conclusions with respect to gross fracture have been made.

Processing techniques have received the widest attention in comparative studies. Thorne and Howard (ref. 32) compared four different types of alumina: medium-density (3.4-g/cm³) flame-sprayed, high-density (3.7-g/cm³) sintered, low-density (2.7-g/cm³) extruded, and low-density (3.0-g/cm³) slip-cast. For the three irradiation temperatures employed (250°, 475°, and 700° C), no significant differences in property changes were found among the four materials after a dose of 10^{21} neutrons/cm². Properties examined included volume expansion, Young's modulus, and thermal conductivity. However, the two denser types were definitely superior to the more porous materials with respect to gross fracture at 700° C. Hickman and Walker (ref. 29) found essentially no difference in expansion between single crystals and various HP and CP/S polycrystalline samples. This was for a dose of 5×10^{20} neutrons/cm² at 75° to 100° C. A limited comparison between CP/S alumina and the high-density translucent form (Lucalox) can be made from the results of Keilholtz, et al. (refs. 27 and 30). Although the two materials had similar volume expansion at about 100° to 300° C and about 1.5×10^{21} neutrons/cm², the experimenters feel that translucent alumina performs better with respect to gross fracture.

As mentioned previously, Thorne and Howard (ref. 32) showed that high-density alumina has a higher fracture threshold than low-density alumina in a test comparing four different processing techniques. This behavior may be due to thermal stress effects arising from the large differences in thermal conductivity between the samples. (These effects will be discussed in a separate section.) Keilholtz, Lee, and Moore

(ref. 30) compared two materials with densities of 3.6 and 3.8 grams per cubic centimeter at 150°C , but found no significant differences in volume expansion to 1.4×10^{21} neutrons/cm². Grain size also seems to have little effect on the radiation behavior of alumina. Hickman and Walker (ref. 29) found no significant difference between two cold-pressed materials with grain size in the range 4 to 6 microns and 40 to 200 microns. This applies to expansion and strength data after irradiation to a dose of 5×10^{20} neutrons/cm² at 75° to 100°C .

The effects of neutron flux and irradiation temperature on property changes in alumina have not been examined to any great extent. In the few tests where different fluxes were used, data are insufficient to draw any conclusions. Temperature data are scarce above 700°C . From the data that do exist, however, one can draw the expected conclusion that property changes are significantly less at higher irradiation temperatures. Desport and Smith's measurements of single crystal volume expansion (ref. 21) showed that expansion of samples irradiated at 150°C was eight times as large as that obtained in a 1000°C irradiation at the same dose. Thorne and Howard (ref. 32) found that changes in expansion and thermal conductivity of polycrystalline materials decreased as the irradiation temperature was increased from 250° to 700°C . Several groups have also measured large decreases in lattice parameter changes at higher irradiation temperatures (e. g., see refs. 29, 30, and 32). Contrary to these data, the results of testing at various temperatures indicate that gross damage (cracking and fracturing) increases with irradiation temperature (refs. 27, 28, 30, and 32).

From the limited amount of data described previously, one could make the following statements which may be helpful in examining the property changes of alumina under irradiation:

- (1) Material variables do not significantly affect property changes.
- (2) Property changes are less for higher irradiation temperatures.
- (3) Temperature and possibly density affect the gross fracture characteristics.

Property Changes Under Irradiation

Gross fracture. - Although gross fracture is not really a physical property, its common occurrence in high-temperature irradiations requires its examination. Keilholtz (ref. 30), after an irradiation of CP/S alumina between 0.5 and 4.8×10^{21} neutrons/cm² at 800° and 1100°C , found that nearly all samples were fractured. By comparison, fracturing occurred in about 50 percent of samples tested at 150°C in the dose range 0.2 to 1.4×10^{21} neutrons/cm². Better results were obtained with high-density translucent alumina (Lucalox) irradiated at temperatures from 300° to 600°C (ref. 28). Of 33 samples, virtually no fracturing occurred below 3×10^{21} neutrons/cm²,

although severe fracturing occurred at higher doses. Thorne and Howard's irradiation (ref. 32) of different types of alumina to doses of 1.6×10^{21} neutrons/cm² produced no cracking at temperatures of 250° and 475° C, but results were not as good at 700° C. Of 26 porous specimens (density less than 3 g/cm³), 19 cracked or disintegrated below 2×10^{20} neutrons/cm², and six below 6×10^{20} neutrons/cm². One survived a dose of 4.6×10^{20} neutrons/cm². The behavior of denser material (density greater than 3.4 g/cm³) at 700° C was better; cracking was not observed until 1.4×10^{21} neutrons/cm².

Volume expansion. - Data on the volume expansion of irradiated alumina are plotted in figures 5 and 6. Figure 5 (from ref. 32) illustrates the effect of irradiation temperature on the expansion. For equivalent doses, expansion at 250° C is about three times that at 700° C. One can also see from the figure that a wide diversity in sample composition does not significantly affect the expansion, as mentioned previously. Figure 6 compares the expansion of various alumina samples including single crystals. Note that the values for crystals and ceramics are quite similar over the dose range examined, and that one data point indicates that crystal expansion at 1000° C is very small compared to that at room temperature. The data for translucent alumina are somewhat puzzling in that they do not exhibit the temperature dependence expected. That is, the expansion of translucent alumina at 300° to 600° C is as large as that of other forms of alumina at 75° to 150° C and similar doses.

Mechanical properties. - Thorne and Howard (ref. 32) measured the dynamic Young's modulus of 12 samples irradiated at 250°, 475°, and 700° C to doses of 1.1 to 12×10^{20} neutrons/cm². Results varied from a 15 percent decrease to a 10 percent increase in the modulus. Hickman and Walker (ref. 29) found 20 to 60 percent increases in fracture strength after a dose of 5×10^{20} neutrons/cm² at 100° C. No correlation with dose or temperature could be drawn from either of these tests.

Thermal properties. - Thorne and Howard (ref. 32) also measured changes in the room-temperature thermal conductivity of various alumina types after irradiation at temperatures of 250°, 475°, and 700° C. The results, plotted in figure 7, show a definite temperature dependence. Changes in room temperature expansion coefficient were also measured on 21 samples receiving neutron doses between 0.7 and 12×10^{20} neutrons/cm². Both decreases and increases were found, the maximum change being about 7 percent. No correlation with dose or temperature (250°, 475°, and 700° C) was found.

Electrical properties. - The influence of both neutrons and gamma radiation on the electrical resistivity of alumina have been studied. Tests examining neutron effects have not been at very high doses, and results are conflicting. Patrick (ref. 22) irradiated several samples at temperatures of 425° to 700° C. Of ten specimens irradiated at lower temperatures (425° to 475° C), five retained their original resistivity of

$\geq 10^9$ ohm-centimeters after a dose of 1.5 to 3.0×10^{20} neutrons/cm². The other had dropped to 10^4 to 10^5 ohm-centimeters. Similar results were obtained on 11 samples irradiated at higher temperatures (625° to 700° C) to about 3×10^{20} neutrons/cm². Eight had resistivities of 10^7 to 10^9 ohm-centimeters (four greater than 10^9 ohm-cm) while the other three dropped to 10^3 to 10^5 ohm-centimeters. Quite different results were obtained by General Electric experimenters (ref. 33) after an irradiation at 800° to 1000° C and doses to 1.8×10^{20} neutrons/cm². Resistivity measurements and breakdown tests were made on eight translucent alumina samples of 30-mil (0.76-mm) thickness at various intervals during the irradiation. The resistivity was generally higher than the pre-irradiation value by as much as a factor of five. Only one sample indicated possible breakdown at the testing voltage of 10 volts per mil (3.94 kV/cm). However, its resistivity was similar to the other samples. The effects of relatively low gamma dose rates on alumina's electrical properties have also been studied by Davis, et al. (refs. 1, 34, and 35). Their results on the resistivity of translucent alumina and commercial flame-sprayed alumina with and without radiation are plotted in figure 8. It can be seen that no discernable effects occur above about 400° C. Separate tests by the same group confirmed that the low-temperature resistivity change is indeed a gamma effect. The relative unimportance of this effect at high temperatures is confirmed for higher dose rates by the GE experiment (ref. 33) described previously. No decreases in resistivity were found during reactor irradiation at 800° to 1000° C. The gamma dose rate, though not reported, must have been relatively high since the fast neutron flux was 3.4 to 4.2×10^{13} neutrons/(cm²)(sec).

RADIATION EFFECTS IN THORIA, ZIRCONIA, AND YTTRIA

Very little useful data could be found on thoria, zirconia, and yttria. Kircher and Bowman (ref. 5), who devote an entire chapter to ceramic materials, do not even mention ThO₂ or Y₂O₃. The latest three "state-of-the-art" reports from the Radiation Effects Information Center (refs. 36 to 38) do not specifically mention any of the three. In general, work that has and is being done is not of particular value in determining behavior of the pure oxides at high doses and temperatures.

Most early work on zirconia dealt with an observed phase change from the monoclinic to the cubic form after irradiation (refs. 5 and 39). This phase change evidently depends mainly on certain impurities or the presence of fission fragments. More recent work affirms that such a change will not occur in pure ZrO₂ from neutrons alone (refs. 40 and 41). Although little high-temperature property change data could be found, reference 5 states that the low-temperature data do not indicate any significant difference from other oxide ceramics. In an examination of the gamma-induced conductivity

of zirconia, Davis (ref. 1) found no significant effect for a dose rate of 5×10^6 roentgens per hour (1.29×10^3 C/(kg)(hr)) above about 200° C.

There is some interest in thoria as a radiation-resistant insulator for thermocouples, but this is generally for temperatures of the order of 2000° C and higher. Any radiation data at this temperature cannot be expected to be valid at the lower temperatures of interest in thermionic systems; therefore, this area was not surveyed. Also of little use are numerous data on combinations of thoria with nuclear fuel materials or other oxides. Davis (ref. 1) has studied the resistivity of thoria along with the other oxides; no radiation effects were found at 5×10^6 roentgens per hour (1.29×10^3 C/(kg)(hr)) above about 300° C.

Very little testing of yttria has been performed. Patrick (ref. 22) found that a sample irradiated at 1.5×10^{20} neutrons/cm² and 425° C was cracked, although the resistivity remained relatively high (1.57×10^9 ohm-cm).

ADDITIONAL TOPICS

The purpose of this section is to discuss certain aspects of irradiation behavior which may serve to supplement or qualify the actual property change experiments described previously. These topics include annealing experiments, analytical work, and the influence of experimental variables and techniques on results.

Annealing Studies

Annealing experiments are those in which the behavior of a radiation-induced property change is examined as the sample is either heated above the irradiation temperature or simply held at its irradiation temperature for long periods of time. Such experiments are primarily used to gain information on basic mechanisms and to formulate analytical expressions. However, they can also provide some insight into or confirmation of high-temperature property changes.

Much work has been done on annealing of irradiated BeO and has helped in understanding the defect structure (e. g., see refs. 7, 11, 15, 23, and 42 to 47). A common result of these studies is a more-or-less linear relation between recovery and temperature, with the persistence of at least part of the damage to high temperatures, often 1400° to 1600° C. Thus one might expect that the improved radiation stability as temperature is increased would also apply to temperatures above about 1000° C. However, little or no irradiation at these higher temperatures has been done as yet.

Dulow, McDonald, and Pryor (ref. 48) have obtained some interesting results on the effects of temperature on the microcracking of BeO. In one test they examined the thermal conductivity at -195°C as a measure of microcracking. Although no annealing was found below 800°C , the recovery was 50 percent at 1000°C and 100 percent at 1200°C , indicating that the material had healed itself. In another series of tests, Hickman, Rotsey, and Veevers (ref. 49) irradiated BeO samples at 600°C to a dose insufficient to cause microcracking and then annealed the samples at either 900°C or 1000°C . The major parameter of interest was the amount of X-ray line broadening. This is known to be a measure of the anisotropic growth strain which is a primary cause of microcracking. Although the annealing temperatures were not high enough to affect the actual lattice expansion, there was considerable annealing of the growth strain. The recovery was much better at 1000°C than at 900°C and was also much better for small grain size (3 to 5 μm as compared with 10 to 12 μm). Re-irradiating the material showed that the internal strains were indeed removed by the annealing; the strength properties after re-irradiation were the same as for samples being irradiated for the first time. Although the mechanism involved is not well understood, it was concluded that periodic annealing of irradiated BeO at 1000°C should extend its life indefinitely in the case of low-temperature irradiations. In addition, no microcracking should occur in irradiations at 900° to 1000°C , although helium bubbles may be a problem here.

Annealing tests on Al_2O_3 have not been as numerous as with BeO, and most tests have involved single crystals instead of polycrystalline samples. Bopp's results (ref. 50) on the thermal conductivity of several ceramics after irradiation to 2×10^{19} neutrons/cm² indicate that the annealing rate of alumina is less than that of beryllia. The alumina conductivity change was only 40 percent recovered at 1050°C , while beryllia had recovered 80 percent at 900°C . Similar behavior was noted by Desport and Smith (ref. 21) in the annealing of alumina and beryllia growth after 3.5 to 4×10^{19} neutrons/cm². There was 85 percent recovery at 1250°C for Al_2O_3 single crystals and at 1000°C for BeO polycrystalline samples. Hickman and Walker (ref. 29) found 65 percent recovery of density change at 1000°C after doses of 4.4, 21, and 50×10^{19} neutrons/cm². This lack of dose dependence is contrary to most BeO results, in which percent recovery was lower for higher doses (e. g., see refs. 21, 43, 44, and 51).

Analytical Work

Due to the complex processes occurring in these oxides, analytical treatment of most property changes is very difficult. Some attempts have been made, however, and have been relatively successful. Collins (ref. 10) has developed an expression for the microscopic expansion of BeO, exclusive of microcracking and helium bubbles. Con-

stants were evaluated from annealing studies, and the resulting equation predicts a saturation of the expansion dependent on neutron flux and temperature. Based on the observation that microcracking occurs at about 0.5 percent microscopic expansion in samples of 20-micron grain size, the following criterion for no microcracking can be obtained from the expression of reference 10:

$$1.08 \times 10^{-16} \Phi e^{5180/T} \leq 1$$

At 1000° C, this reduces to $\Phi \leq 1.4 \times 10^{14}$ neutrons/(cm²)(sec). One would expect smaller grain sizes to show even higher flux thresholds since microcracking begins at a larger microscopic expansion in this case.

An expression which treats the actual macroscopic volume expansion of BeO has been developed by Pryor and Hickman (ref. 12). The various parameters in the theory were evaluated by fitting the expression to existing data. At reasonably long times ($\geq 10^7$ sec), the equation reduces to

$$\frac{\Delta V}{V} = 4.9 \times 10^{-14} \Phi \left(1 - e^{-A_{vs}t} \right)$$

where $\Delta V/V$ is given in percent and

$$A_{vs} = 2 \times 10^7 \text{ sec}^{-1} e^{-3.8/kT}$$

At a temperature of 1000° C and a dose of 10^{22} neutrons/cm², this predicts an expansion of about 4.1 percent at a flux of 10^{14} neutrons/(cm²)(sec) ($t = 10^8$ sec) and about 5.8 percent at 2×10^{14} neutrons/(cm²)(sec) ($t = 5 \times 10^7$ sec).

Clarke and Wilks (refs. 11 and 52) have done some analytical work on the mechanical properties of irradiated BeO. Their model predicts that the neutron dose at which microcracking first occurs should vary as (grain size)^{-1/2}. The grain-size relation was shown to fit experimental data quite well over a range of about 1 to 100 microns.

Gamma-induced conductivity in oxides has been treated analytically by Davis, et al. (refs. 1, 34, 35, 53, 54, and 55). They have shown that the conductivity at a particular temperature in a gamma field is equal to the out-of-pile conductivity plus a correction term $\sigma(P)$. They found this term to be of the form:

$$\sigma(P) = A P T^{3/2} \exp(-U/kT)$$

where A is a normalization constant and U is an electron "trap depth" energy for a

particular oxide (ref. 1). Reference 35 gives the following values for alumina:

$$A = 7.4 \times 10^{-21} (\text{ohm}^{-1} - \text{cm}^{-1}) (^{\circ}\text{K}^{-3/2}) (\text{R}^{-1}) (\text{hr})$$

$$\text{or } 2.87 \times 10^{-17} (\text{ohm}^{-1} - \text{cm}^{-1}) (^{\circ}\text{K}^{-3/2}) (\text{C}^{-1}) (\text{kg}) (\text{hr})$$

and

$$U = 0.086 \pm 0.014 \text{ eV} (1.38 \pm 0.22 \times 10^{-20} \text{ J})$$

Using these values and a temperature of 1000°C results in a value for $\sigma(\text{P})$ of $1.54 \times 10^{-7} \text{ ohm}^{-1} - \text{centimeter}^{-1}$ for a dose rate of 10^9 roentgens per hour ($2.58 \times 10^5 \text{ C}/(\text{kg})(\text{hr})$). Since the normal conductivity of alumina is higher than this (depending on impurities), it is seen that the equation predicts no significant effects from gamma radiation. The same is also probably true for other oxides, since experimental work (ref. 1) showed that $\sigma(\text{P})$ is about the same for Al_2O_3 , BeO , ThO_2 , and ZrO_2 , at least at 5×10^6 roentgens per hour ($1.29 \times 10^3 \text{ C}/(\text{kg})(\text{hr})$).

Thermal Stress Effects in Reactor Testing

This section will discuss the influence of thermal stress and thermal cycling on the radiation properties of the oxides, primarily with respect to gross fracture and micro-cracking. Although these thermal effects result from the radiation environment, they will be treated separately from actual radiation-induced property changes. This is because they are also quite dependent on such experimental variables as reactor cycling characteristics and sample dimensions, and so the effects might be absent in some applications.

The thermal stress in a cylindrical sample is given by $\alpha E(T_a - T_s)/(1 - \gamma)$, where the temperature difference is proportional to Qr^2/K . This shows the relative importance of sample size and temperature, the latter because of the large decrease of thermal conductivity with temperature (see table I). One may also use the equation to compare the stress resistance of the various oxides.

The role of thermal stress in the reactor experiments described previously is often difficult to evaluate because the gamma heating rates are seldom given. However, some experimenters have shown that thermal stress must be considered. Shields, Lee, and Browning (ref. 56) showed that the maximum thermal stress from steady-state gamma heating exceeded the tensile strength of BeO for sample diameters greater than about 0.5 inch (1.27 cm). This was for a heating rate of 25 watts per gram at 900°C . Tobin

(ref. 20), in order to keep thermal stresses low, chose a sample diameter of 1/4 inch (0.635 cm). This resulted in a calculated stress of about 1100 pounds per square inch ($7.59 \times 10^6 \text{ N/m}^2$ - about one-tenth the tensile strength) for a heating rate of 15 watts per gram at about 900°C . The previous calculations indicate that for the gamma heating normally encountered in reactor testing, some thermal fractures may be expected in 1/2-inch-diameter (1.27-cm-diam.) samples at high temperatures, while 1/4-inch (0.635-cm) samples seem to be relatively safe. This applies only to steady-state operation, however, assuming values for the pertinent properties before irradiation.

It is possible that thermal stress cracking can occur even where initial calculations indicate that the stresses are below the strength of the material. One of the reasons for this is the increased stress during cooldown after irradiation. Collins (ref. 9) has found that some nonmicrocracked BeO specimens began to show microcracking during cooldown, and specimens that were already microcracked became even more so. This was for <1/4-inch (0.635-cm) samples. Keilholtz, Lee, and Moore (ref. 18) have postulated that the number of reactor cycles may also be important. They found more microcracking in BeO specimens irradiated at lower fluxes than those receiving an equal dose at a higher flux. This was attributed to the fact that the low-flux tests required three times as many reactor cycles, which promoted grain-boundary separation.

Another possible cause of increased thermal stress during testing is the change in an important property because of radiation. An increase in elastic modulus or a decrease in thermal conductivity or strength will increase the possibility of thermal stress fracture. Such an occurrence could explain the sudden gross fracturing of specimens which had previously withstood many reactor cycles with only small changes. This theory is confirmed to some extent by experimental results. Hickman and Pryor (ref. 7) found evidence of thermally induced cracking in low-temperature tests with BeO after radiation-induced microcracking occurred, but not before. This correlates with the evidence that the conductivity of BeO drops sharply after microcracking occurs. Some interesting results were also obtained by Thorne and Howard (ref. 32). They found that denser Al_2O_3 specimens withstood five times the dose before cracking as opposed to more porous samples. The dense materials had twice as high a value for thermal conductivity before irradiation. The threshold dose for fracture correlates with the measured decrease in thermal conductivity with dose.

In conclusion, it may be said that great care must be used in applying results of reactor tests of a particular oxide to all radiation applications of that oxide. This is especially true of gross fracture results in all oxides and microcracking in beryllia. It is seen that sample size, reactor cycling, and temperature may be important in determining thermal stress resistance.

CONCLUDING REMARKS

The large amount of radiation damage work on BeO has resulted in several well-founded criteria for better radiation stability, even though the damage mechanisms are still disputed. The most important of these are:

1. Smaller grain size raises the dose at which grain-boundary separation begins.
2. Low density (2.5 to 2.7 g/cm^3) reduces radiation-induced volume expansion.
3. Cold-pressed/sintered or extruded/sintered samples perform better than hot-pressed types.
4. Small amounts of certain additives can improve resistance to microcracking.

Beryllia samples with the stated characteristics have been successfully tested to a neutron dose of 9×10^{21} neutrons per square centimeter (neutrons/cm^2) at 1000°C . Changes in dimensions and strength were relatively minor considering the magnitude of the dose involved. Other results, although at lower doses, indicate that thermal and electrical property changes will not be overly large either. An additional consideration for thermionic application is the influence of helium production and subsequent release into the interelectrode gap, which may adversely affect converter performance.

Alumina tests, on the other hand, have not been as extensive nor as successful as those with beryllia. High-dose, high-temperature tests have been characterized by gross cracking, and not much property data are available. Comparison of lower temperature results on alumina and beryllia does not explain the cracking, however. In general, for equivalent doses, property changes in alumina are no worse, and in many cases less severe than in beryllia. A possible explanation for this apparent discrepancy may be the thermal stresses induced during various phases of reactor testing. Beryllia is known to have much better thermal shock resistance than other oxides. It is possible that high-conductivity, high-strength alumina samples of smaller dimensions may perform as well as beryllia at 1000°C .

Data on thoria, zirconia, and yttria are insufficient to determine high-temperature behavior. Little high-temperature basic studies have been made on these oxides.

In conclusion, results to date indicate that beryllia would perform best at a temperature of 1000°C at doses to 10^{22} neutrons/ cm^2 . This does not mean to say that the others will not perform as well, but that experimental verification has not been obtained as yet.

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TABLE I. - PHYSICAL PROPERTIES OF CERAMIC INSULATOR MATERIALS AT VARIOUS TEMPERATURES

[From refs. 1, 4, 57 to 61.]

Mate- rial	Thermal expansion coefficient, °K ⁻¹	Electrical resistivity, ρ, ohm-cm	Thermal conductivity, K		Tensile strength		Modulus of elasticity, E		
			Btu/(hr)(ft)(°F)	W/(m)(°K)	psi	N/m ²	psi	N/m ²	
Room Temperature									
Al ₂ O ₃	-----	<div><div>> 10¹⁴</div><div>↓</div></div>	20-23	35-40	37-40×10 ³	26-28×10 ⁷	44-55×10 ⁶	30-38×10 ¹⁰	
BeO	-----		105-160	180-280	12-19	8-13	38-60	26-41	
ThO ₂	-----		7.6-8.9	13.1-15.4	14	10	20-35	14-24	
ZrO ₂	-----		0.95	1.65	21	14	20-25	14-17	
Y ₂ O ₃	-----		9.2	16	-----	-----	-----	-----	
500° C									
Al ₂ O ₃	5-9×10 ⁻⁶	3×10 ⁸ -10 ¹¹	6-7	10-12	36×10 ³	25×10 ⁷	42-52×10 ⁶	29-36×10 ¹⁰	
BeO	7-9.5	10 ⁹ -10 ¹⁰	32-47	55-81	11-18	7-12	36-57	25-39	
ThO ₂	8-10	10 ⁸	3.0-3.7	5.2-6.4	-----	-----	18-33	12-23	
ZrO ₂	8-10	3×10 ⁵ -10 ⁷	1.0	1.8	19	13	18-24	12-16	
Y ₂ O ₃	8-12	a4×10 ⁷ -10 ¹⁰	2.8	4.8	-----	-----	-----	-----	
1000° C									
Al ₂ O ₃	7-10×10 ⁻⁶	3×10 ⁴ -10 ⁷	3.2-4.2	5.5-7.3	34×10 ³	23×10 ⁷	38-46×10 ⁶	26-32×10 ¹⁰	
BeO	8-10	10 ⁷	12-20	20-35	4-12	3-8	31-53	21-37	
ThO ₂	8.5-10.5	10 ⁴ -10 ⁵	1.8-2.3	3.1-4.0	-----	-----	16-30	11-21	
ZrO ₂	8-10	10 ³ -10 ⁵	1.1	1.9	15	10	15-21	10-14	
Y ₂ O ₃	8.5-12	10 ³ -10 ⁵	1.6	2.8	-----	-----	26	18	

^aEstimated from other temperatures.

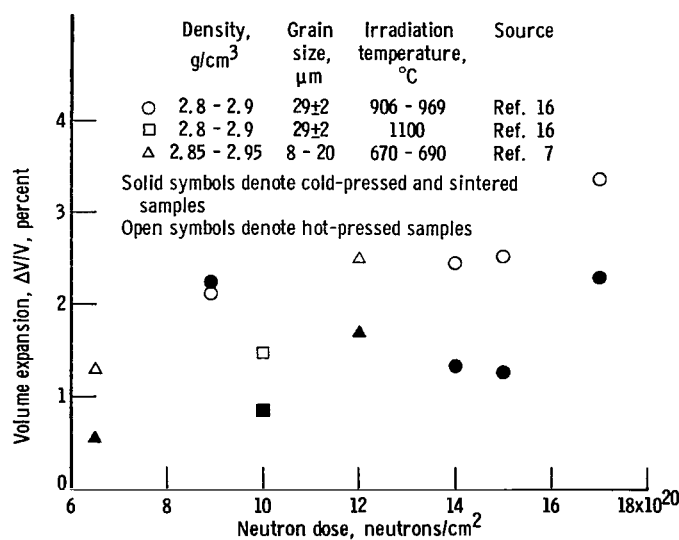


Figure 1. - Effects of radiation on BeO volume expansion for different processing techniques.

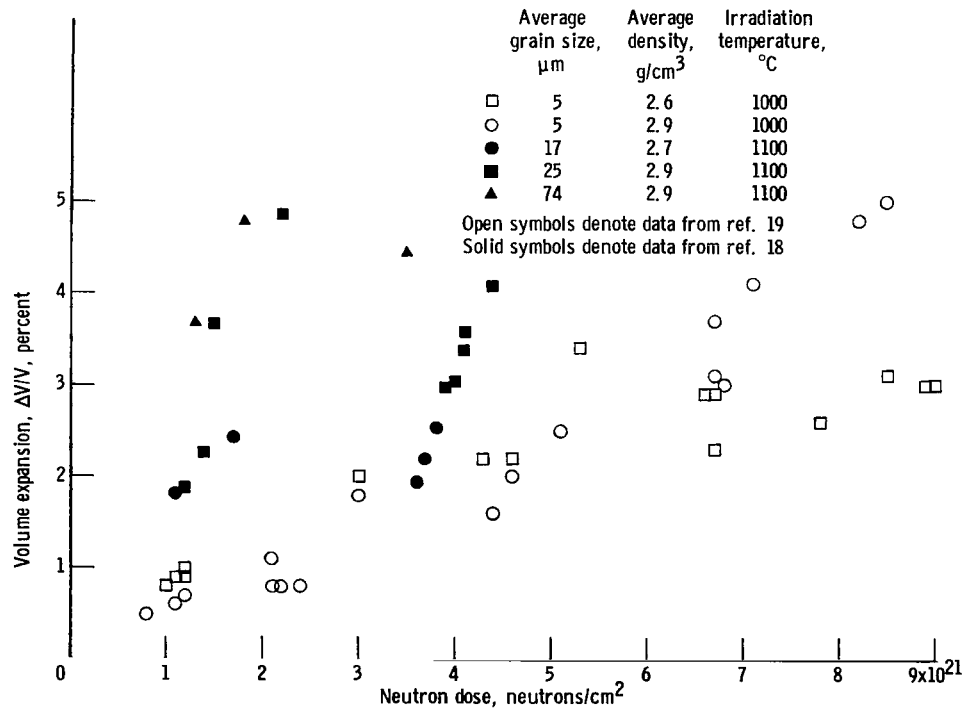


Figure 2. - Effects of radiation on BeO volume expansion at high temperatures.

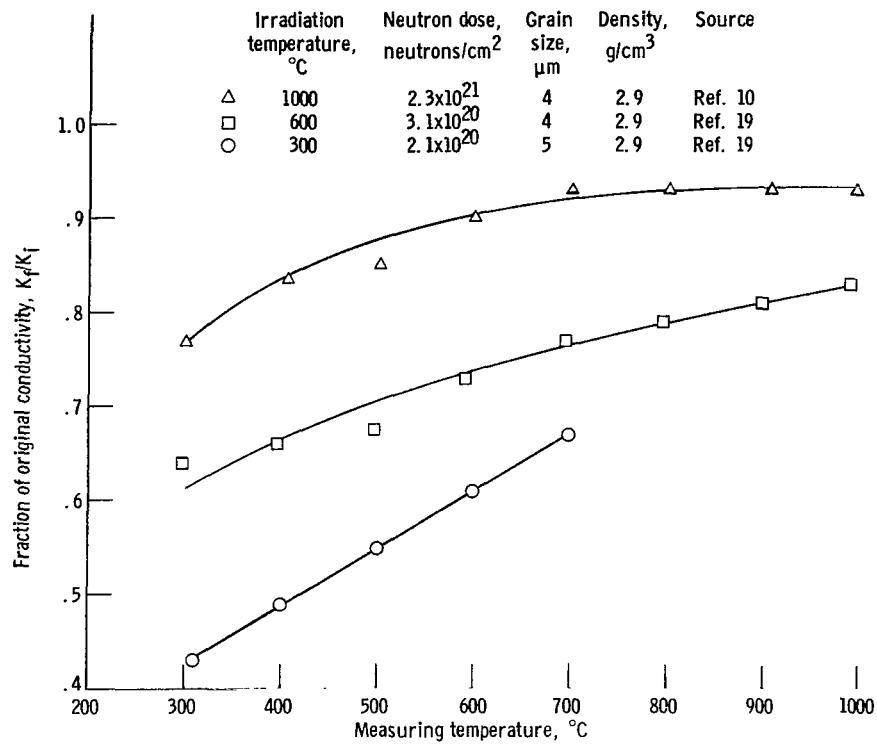


Figure 3. - BeO thermal conductivity as a function of temperature after irradiation at various temperatures.

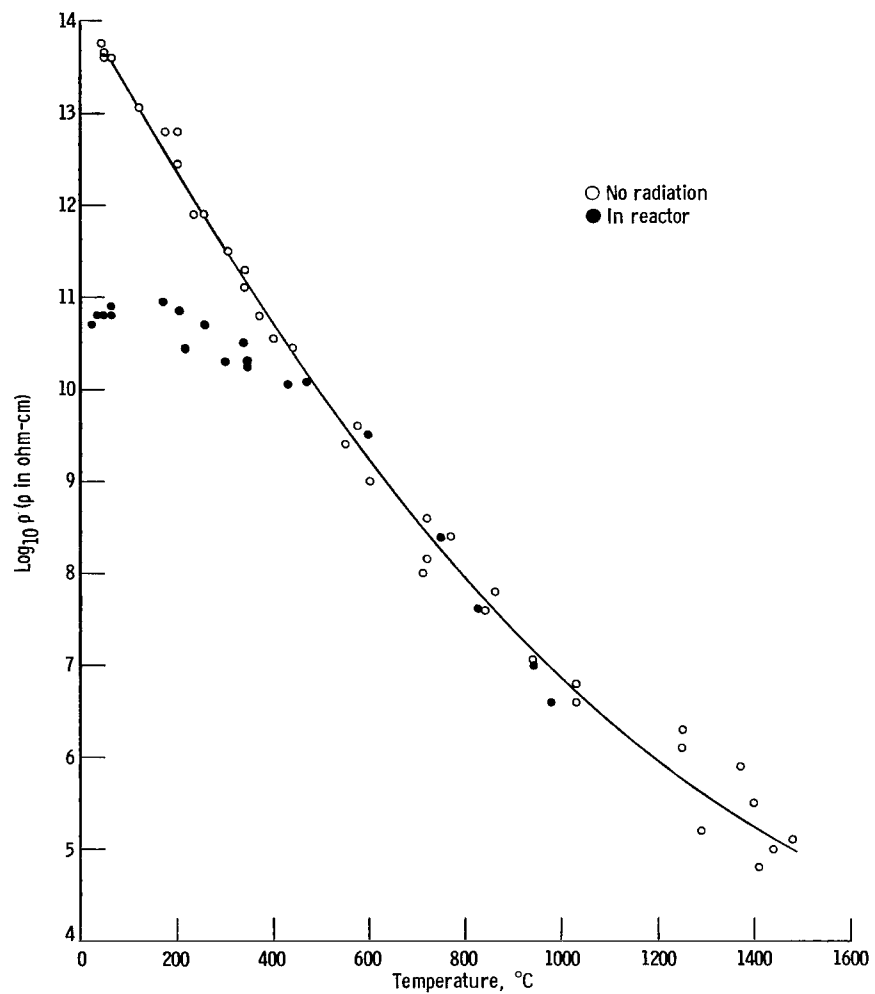


Figure 4. - BeO resistivity as a function of temperature for no radiation and in reactor gamma field of 5×10^6 roentgens per hour (1.29×10^3 C/(kg)(hr)) (from ref. 1).

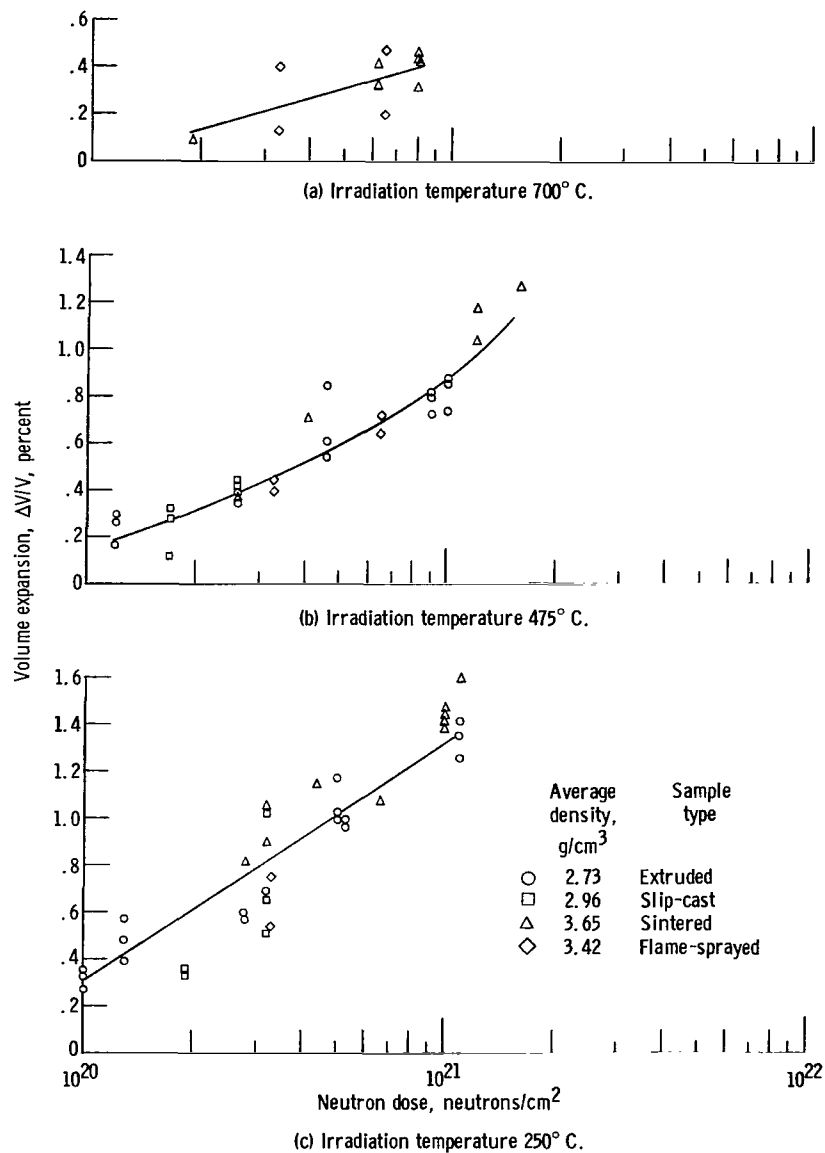


Figure 5. - Effects of radiation on Al_2O_3 volume expansion at various temperatures (from ref. 32).

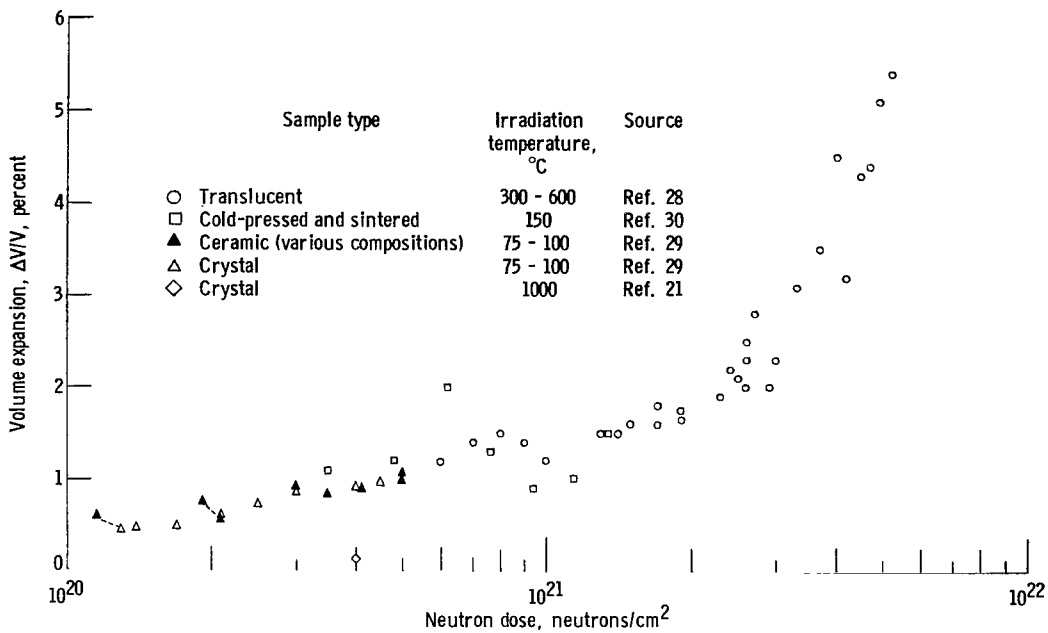


Figure 6. - Effects of radiation on Al_2O_3 volume expansion.

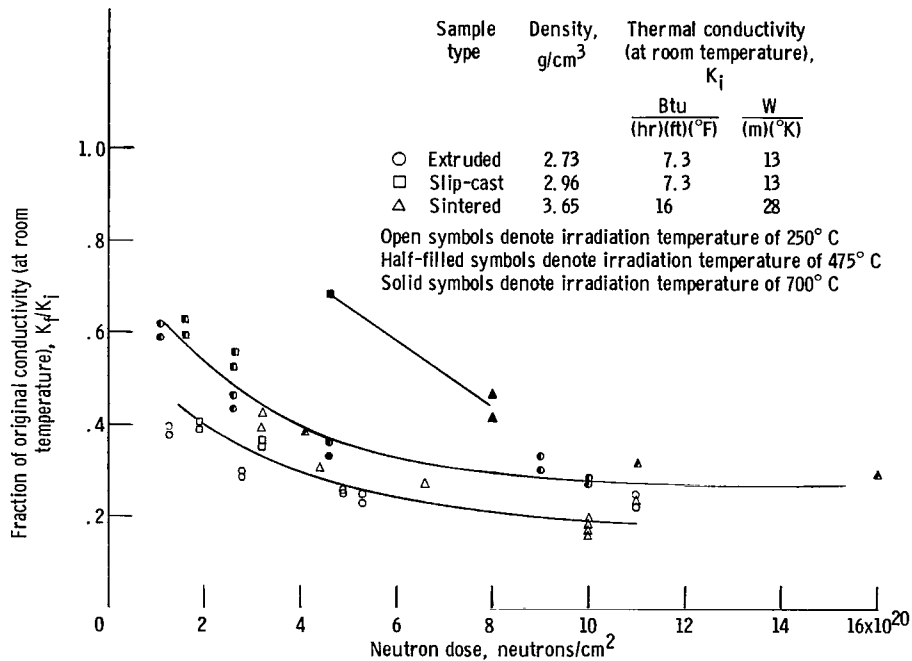


Figure 7. - Effects of radiation on Al_2O_3 thermal conductivity at room temperature (from ref. 32).

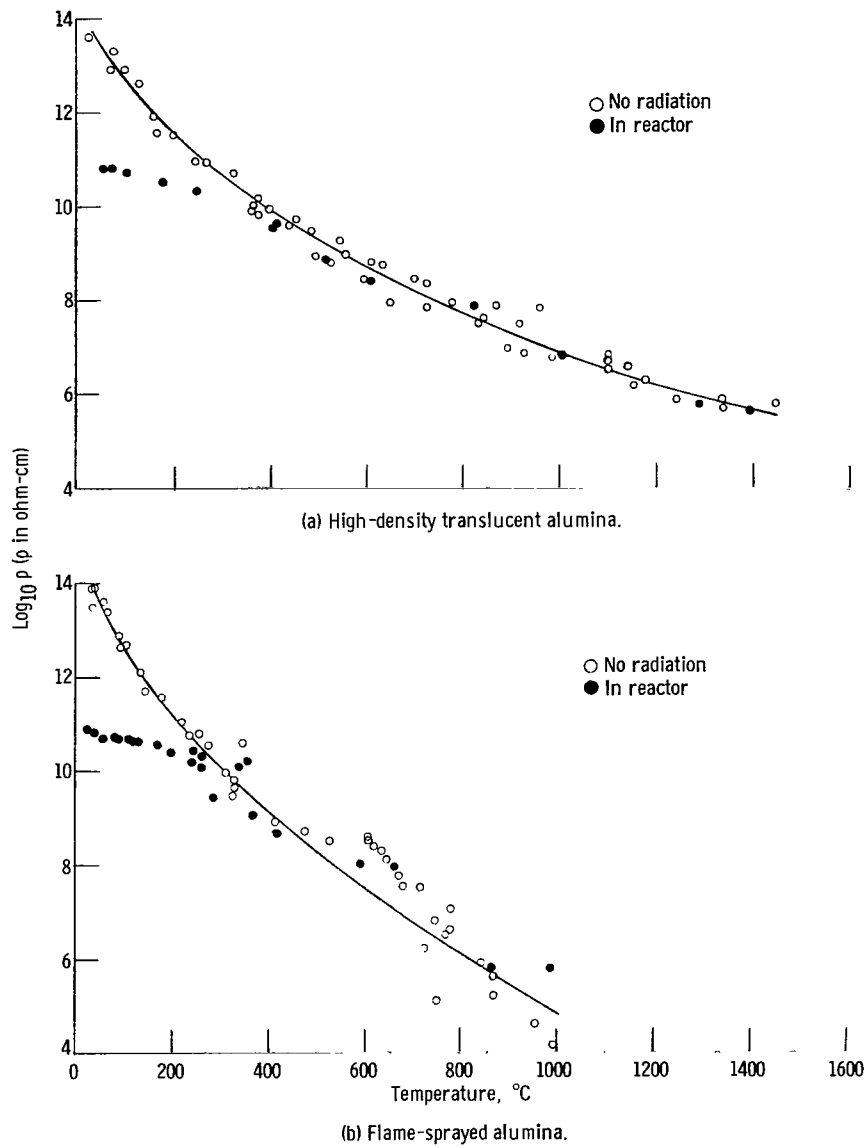


Figure 8. - Al_2O_3 resistivity as a function of temperature for no radiation and in gamma field of 5×10^6 roentgens per hour ($1.29 \times 10^3 \text{ C}/(\text{kg})(\text{hr})$) (from ref. 1).

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